Origin of the multiferroic-like properties of Er_2CoMnO_6

J. Blasco[1*], G. Subías[1], J. García[1], J. Stankiewicz[1], J. A. Rodríguez-Velamazán[1,2], C. Ritter[2] and J. L. García-Muñoz[3]

[1]Instituto de Ciencia de Materiales de Aragón, Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain
[2]Institut de Ciència de Materials de Barcelona, CSIC, Campus univ. de Bellaterra, E-08193 Bellaterra, Spain
[3]Institute Laue Langevin, BP 156, 38042 Grenoble Cedex 9, France
*e-mail: jbc@unizar.es

Introduction.

✓Perovskites with heavy rare earth offer an excellent opportunity to develop new multiferroic materials as several mechanisms combining ferromagnetism and ferroelectricity can be operative in these systems.

✓ First principles density-functional theory calculations predicted an E-type magnetic ground state for double perovskites with heavy rare earth atoms [1,2]. The E-type magnetic arrangement ↑↑↓↓ breaks the inversion symmetry and allows for a ferroelectric polarization perpendicular to the chain direction. This magnetic ordering, coupled to the formation of electric dipoles, was proposed to explain the electric polarization experiments in both Y_2CoMnO_6 [2,3] and $SmCoMnO_6$ [4]. We note that the electric polarization was obtained from measurements of the pyroelectric effect and that the actual magnetic ground state had not been precisely determined.

✓Recently, we have performed a comprehensive study of Yb_2CoMnO_6 [5] and Y_2CoMnO_6 [6] compounds. The former shows an E-type ordering along the z-direction but no electric polarization coupled to the magnetic order was found. The latter shows an collinear ferromagnetic arrangement and we have observed that the pyroelectric current is created through the reorientation of defect dipoles giving rise to thermally stimulated depolarization current (TSDC).

✓Here we present a thorough characterization of the Er_2CoMnO_6 double perovskite. Er^{3+} has a slightly larger size than Yb^{3+} so E-type ordering cannot be excluded. The macroscopic characterization of this sample has shown the occurrence of spontaneous magnetization and electric polarization at low temperature. In this work we focus our study on the origin of this multiferroic behavior that could be very general in the family of double perovskites.

Experimental section.

✓Er_2CoMnO_6 was prepared by solid state reaction of Er_2O_3, Mn_2O_3 and CoO in air at 1250ºC followed by a very slow cooling (0.1ºC/m) in order to improve the Co/Mn ordering [7]. X-ray patterns agree with a single phase.

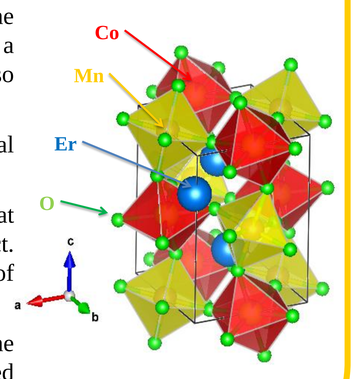
✓Neutron powder diffraction measurements were performed at the ILL using the high intensity D1B (λ=2.52 Å) and high resolution D2B (λ=1.59Å) diffractometers between 1.75 and 295 K.

✓Rietveld refinements of the patterns were carried out using the Fullprof program. The refinement at 295 K (paramagnetic phase) agrees with a double perovskite structure with a monoclinic distortion ($P2_1/n$ space group). The antisites (misplaced cations) were also refined yielding a value of 6%, ie a nearly perfect Co/Mn order (see Fig. on the right).

✓Magnetic measurements were performed between 5 and 300 K by using a commercial SQUID magnetometer.

✓ Dielectric measurements were carried out as a function of temperature in a He cryostat in sintered discs (d=7.9 mm; l=0.95 mm). Silver paint was applied for electrical contact. An impedance analyzer applying voltages with amplitude of 1 V in the frequency range of 10 Hz -5 MHz was used.

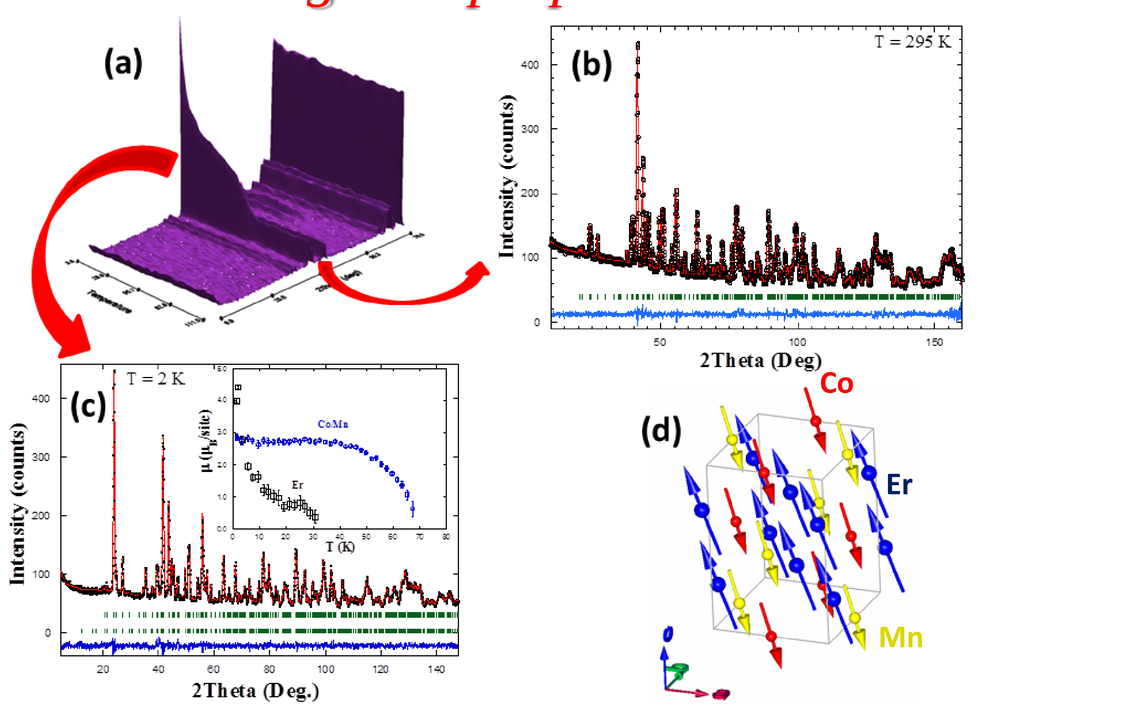
✓ Pyroelectric current was measured with a Keithley 2635B electrometer by warming the sample at a constant rate (1-10 K/min). The change in electrical polarization was obtained by integrating the pyroelectric current as a function of time. Different poling fields were tested.



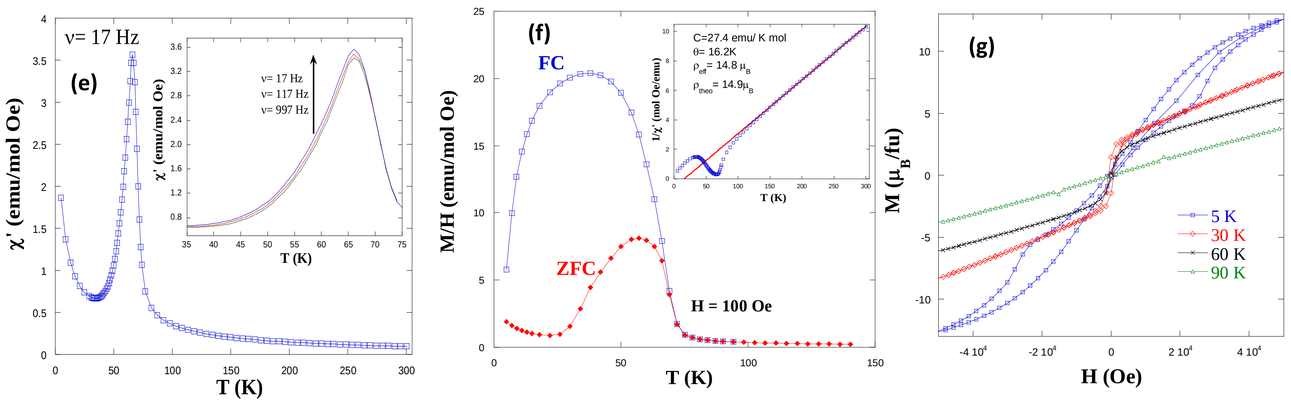
Crystal structure: Monoclinic ($P2_1/n$)
(2*c*) site: 94% Mn + 6% Co
(2*d*) site: 94% Co+ 6% Mn

Results.

Magnetic properties

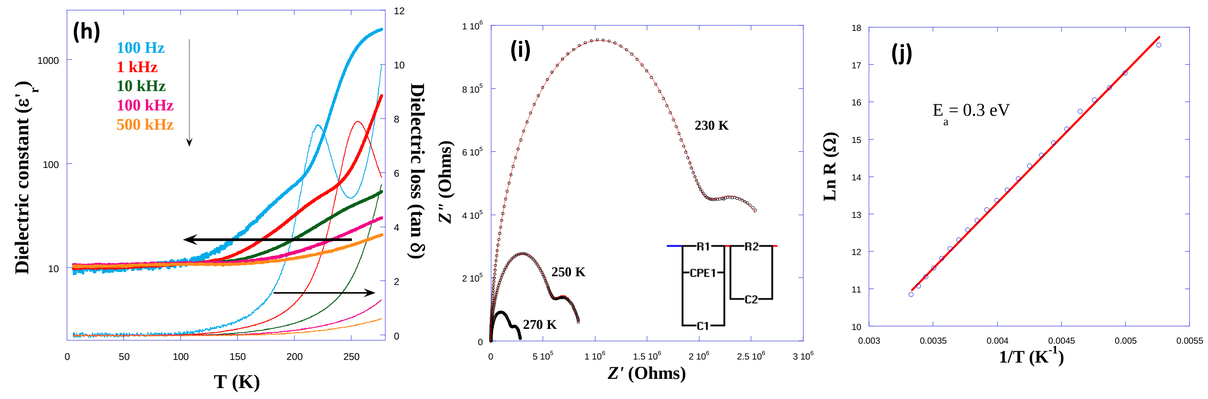


✓(a) Neutron thermodiffractograms (D1B) showing two magnetic transitions at ~70 and ~30 K. (b) Refinement of neutron pattern at 295 K showing a single phase (double perovskite). (c) Refinement of neutron pattern at 2 K with a magnetic contribution arising from the ferromagnetic coupling of Mn^{4+} and Co^{2+} moments, antiferromagnetically coupled to Er^{3+} moments. Inset: Temperature dependence of the ordered moments. (d) Picture of the magnetic structure showing a collinear arrangement (**k**=0) in the ac-plane.

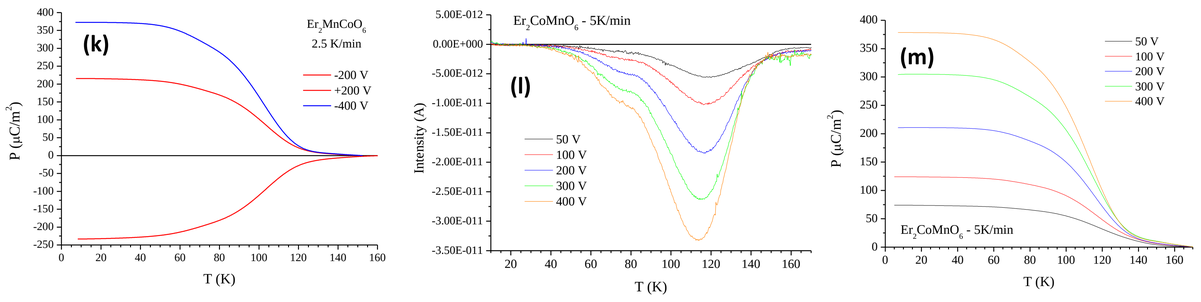


✓(e) The ac magnetic susceptibility shows a sharp peak at the magnetic transition at T_C=66 K. Inset: The amplitude of the peak shows a slight dependence on frequency of the ac field but no significant shift of its position is detected. (f) The dc magnetization under a magnetic field of 100 Oe in zero-field cooled (ZFC) and field-cooled (FC) conditions. There is a strong magnetic irreversibility. The ZFC branch shows a broad peak centered at ~57 K while the FC branch displays a ferromagnetic-like transition at ~68 K (inflection point) and a subsequent decrease at temperatures below 30 K which matches with the onset of the magnetic ordering in the Er-sublattice. Inset: Above the transition temperature, the sample is a paramagnet obeying the Curie-Weiss law in a wide temperature range. The effective paramagnetic moments agree with the expected from Er^{3+}, Mn^{4+} and Co^{2+} cations. (g) Hysteresis loops at the indicated temperatures. The loops at 30 and 60 K show the ferromagnetic coupling between Mn^{4+} and Co^{2+}. At 5 K, the magnetic contribution from Er^{3+} is the strongest. The step-like anomaly at H=25 kOe indicates a metamagnetic transition with a reorientation of the Er moments from antiparallel to parallel to the Co/Mn moments.

Electrical properties

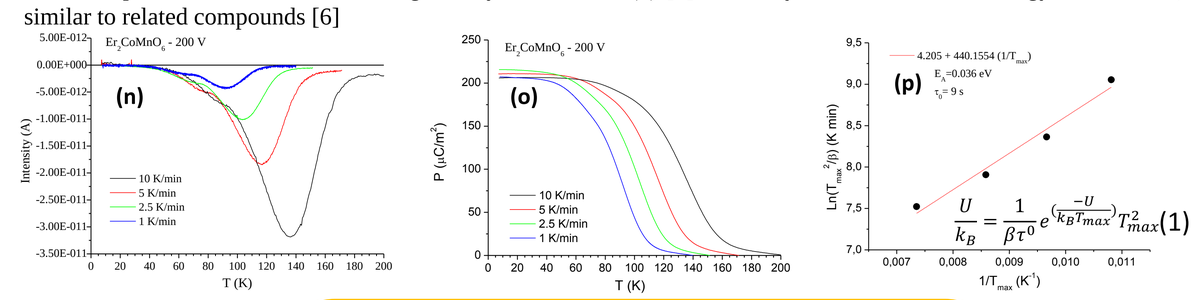


✓(h) The dielectric permittivity (ε'_r) exhibits a step-like increase from a low-temperature value of ~10 to huge values of ~10^3 at 300 K. The dielectric loss factor (tanδ) shows a peak coupled to the step in ε'_r-T curve. These features are shifted to higher temperature as frequency increases which is ascribed to Maxwell-Wagner type contributions of depletion layers. (i) Ac impedance spectroscopy measurements between 10 and 10^7 Hz. The Nyquist plots are composed of two semicircles that are ascribed to different contributions: the first semicircle beginning at the origin of the plot is associated to the bulk properties of the sample and the second one is connected with extrinsic features. (j) The impedance analysis allows us to extract the bulk resistance that displays an activated behavior. The straight line represents the fit to an Arrhenius law.



✓(k) Er_2CoMnO_6 shows electric polarization at low temperature which is reverted by reverting the poling field. (l) Examples of the pyroelectric current measured on heating at a constant rate after cooling the sample with an applied electric field. Two contributions or peaks are clearly noticeable. (m) Electric polarization obtained after integrating the previous curves. There is a linear relationship between poling field and polarization value.

✓(n) Pyroelectric current obtained after heating at different rates. The peaks are shifted to higher temperatures with increasing the heating rate. (o) The corresponding P-T curves exhibit the shift of the critical temperature following the heating rate. This behavior is not characteristic of a true ferroelectric ordering. Instead, it is ascribed to either the reorientation of dipole defects or the release of trapped charges [8,9] giving rise to TSDC. (p) The temperature position of TSDC peaks is related to the heating rate by the formula (1) [9]. The fit yields an activation energy of 0.036 eV, similar to related compounds [6]



Conclusions

✓Er_2CoMnO_6 double perovskite can be prepared with a high cationic order degree and this compound exhibits spontaneous magnetization at T_C~70 K and electric polarization below ~150 K.

✓Spontaneous magnetization comes from the ferromagnetic ordering of Co/Mn sublattice due to the ferromagnetic Co^{2+}-O-Mn^{4+} superexchange interaction. The magnetic structure is collinear with **k**=0 and this result evidences that the occurrence of the E-type order is more difficult to achieve in rare earth double perovskites than initially predicted by theoretical calculations.

✓At 30 K, the magnetic ordering of the Er^{3+} sublattice, which is antiferromagnetically coupled to Co/Mn sublattice, starts. However, an external magnetic field of around 25 kOe is able to induce an spin reorientation giving rise to a ferromagnetic coupling between both sublattices.

✓The dielectric permittivity of Er_2CoMnO_6 does not show any anomaly associated to the occurrence of electric polarization. Its behavior suggests the presence of depletion layers and a significant electron conduction at high temperatures.

✓A thorough study of the pyroelectric effect reveals a dependence on the heating rate typical of TSDC. Thus, the electric polarization is ascribed to reorientation of defect dipoles or release of trapped charges and this feature seems to be very common in ceramic oxides [6,8,9]. Er_2CoMnO_6 is not an intrinsic ferroelectric and therefore not an intrinsic multiferroic.

References:

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